

Biomass-Derived Hydrogen from a Thermally Ballasted Gasifier

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Objectives

- Determine whether switchgrass is a suitable fuel for the ballasted gasifier.
- Obtain time-resolved concentrations of important fuel components evolved.
- Identify process conditions that maximize the production of hydrogen.
- Evaluate methods for removing contaminants from the producer gas.
- Evaluate methods for mediating the water-gas shift reaction in the product gas.
- Estimate the economics of hydrogen production from switchgrass.

Technical Barriers

This project addresses the following technical barrier from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- G. Efficiency of Gasification, Pyrolysis, and Reforming Technology

Approach

- Prepare switchgrass fuel and feeder.
- Prepare 5-ton per day bubbling fluidized bed gasifier and a latent heat ballasting system.
- Prepare slipstream for upgrading producer gas.
- Prepare gas sampling and analysis system.
- Perform gasification trials.
- Perform cost estimate of the gasification system.

Accomplishments

- Established analytical methods for accurate and repeatable measurements of H₂S and NH₃.
- Characterized producer gas from gasification of switchgrass.
- Achieved reductions of 95% in total tar and 99% reductions in condensable (heavy) tar by steam reforming.
- Reduced CO in producer gas to less than 0.5 vol-% by water-gas shift reaction.
- Demonstrated operation of ballasted gasifier in production of raw producer gas with hydrogen concentrations averaging 20 vol-% (before gas upgrading).

- Simulated performance of ballast system through thermal modeling.
- Identified technology for separating hydrogen from carbon dioxide.

Future Directions

- Improve the overall cold-gas efficiency of the gasifier.
- Establish methodology for reliable HCl measurements.
- Demonstrate a combined particulate matter/trace contaminant control system.
- Evaluate the feasibility of a combined catalytic reaction/carbon dioxide sorbent system.
- Perform economic assessment of ballasted gasifier system.

Introduction

The goal of this project is to optimize performance of an indirectly heated gasification system that converts switchgrass into hydrogen-rich gas suitable for powering fuel cells. We have developed a thermally ballasted gasifier that uses a single reactor for both combustion and pyrolysis. Instead of spatially separating these processes, they are temporally isolated. The producer gas is diluted neither with nitrogen nor the products of combustion. The heat released during combustion at 850°C is stored as latent heat in the form of molten salt sealed in tubes immersed in the fluidized bed. During the pyrolysis phase, which occurs at temperatures between 600 and 850°C, the reactor is fluidized with steam or recycled producer gas rather than air. Heat stored in the phase change material is released during this phase of the cycle to support the endothermic reactions of the pyrolysis stage.

Because air is not used during the gas-producing phase of the cycle, nitrogen does not dilute the product gas, resulting in relatively high concentrations of hydrogen and carbon monoxide in the producer gas compared to conventional gasifiers. The carbon monoxide, along with steam used to fluidize the reactor, can be shifted to additional hydrogen by the water-gas shift reaction.

Approach

The approach to this project is to employ a pilot-scale (5-ton per day) gasifier to evaluate the thermally ballasted gasifier as a means for producing hydrogen from switchgrass. Gasification at the pilot scale is important for obtaining realistic process data,

especially for calculating energy flows through the system and assessing the practicality of feeding switchgrass into the gasifier.

A slipstream from the gasifier is used to evaluate gas cleaning and upgrading options. This slipstream includes: a guard bed designed to remove hydrogen sulfide and hydrogen chloride and some tar; a steam reformer designed to crack the remaining tar and decompose ammonia; and high-temperature and low-temperature catalytic water-gas shift reactors to remove carbon monoxide from the product gas and increase its hydrogen content. A series of gasification trials are being performed to evaluate the effectiveness of these four reactors in removing tar and contaminants, and shifting producer gas towards increased hydrogen and decreased carbon monoxide.

Results

Figure 1 illustrates the slipstream system developed for use with the ballasted gasifier. The slipstream system extracts hot producer gas from the exhaust duct at volumetric flow rates (4.5 – 5.5 L/min) appropriate to isokinetic sampling requirements. This gas sample passes through a heated particulate filter maintained at 450°C to prevent condensation of tars; thus, the collected particulate sample can be used to calculate particulate matter concentrations in the producer gas (typically about 10 g/scm). The particulate-free sample then passes through a guard bed of calcined dolomite that removes hydrogen sulfide and hydrogen chloride prior to passage through metal catalysts that would otherwise be poisoned by these trace contaminants. Steam is added at a level appropriate to steam reforming of tar over a nickel

catalyst contained in the second of the four reactors. A high temperature shift reactor and a low temperature shift reactor follow the tar cracker with the purpose of shifting CO and steam to hydrogen and CO₂.

Table 1 summarizes both the operating conditions and results of gas conditioning trials on producer gas generated from air-blown gasification of switchgrass. The “tar cracker” operating in conjunction with the guard bed was able to remove >99% of condensable (heavy) tars from the raw producer gas. Further details of the operation of the tar cracker are found in Reference 1. The combination of water-gas shift reactors reduced CO concentration from 20.1 vol-% to 0.18 vol-%. The outlet concentration of hydrogen was 27.1 vol-%. Further details on the performance of the shift reactors are found in References 2 and 3.

Figure 1 also illustrates the gas sampling system developed for use with the ballasted gasifier, which is separate from the slipstream containing the catalytic

reactors. Heated thimble filters remove particulate matter while a tar condenser, operated slightly above 100°C, removes tar without condensing water (an important consideration in accurately sampling water-soluble trace contaminants). The sample stream is split into two streams. One stream goes to a

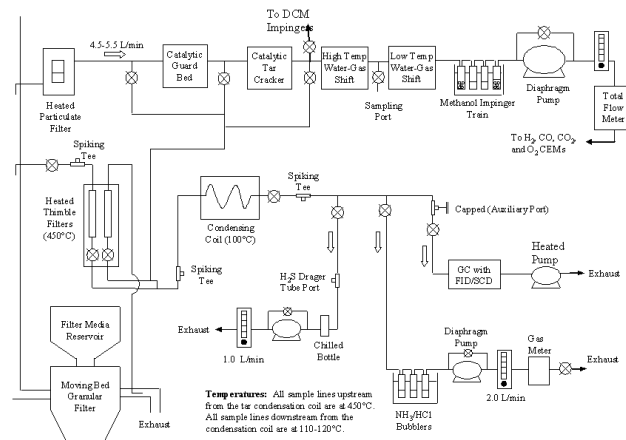


Figure 1. Overall Schematic of Gas Sampling System and Slipstream From Gasifier Effluent

Table 1: Summary of Gas Conditioning Trials on Switchgrass-Derived Producer Gas

Reactor	Guard Bed	Tar Reactor	High Temperature Shift	Low Temperature Shift
Set point temperature of reactor (°C)	650	800	400	200
Temperature range of reactor (°C)	600-670	750-850	350-420	180-240
SV (h ⁻¹)	900	3000	1500	1200
Catalyst	Calcined dolomite	ICI 46-1	Fr-Cr based LB	Cu-Zn-Al based B202
Catalyst volume (ml)	200	60	120	150
Gas Composition*	Inlet gas	Outlet gas	Outlet gas	Outlet gas
H ₂	8.5	19.44	23.7	27.1
CO	14.5	8.9	1.37	0.18
CO ₂	18.1	20.1	26.8	27.2
CH ₄	4.3	3.5	3.4	3.1
C ₂ H ₄	1.5	0.27	0.31	0.13
Tar content (g/Nm ³)	19.5	**	**	**

*Gas composition is dry basis (vol-%) measured by gas chromatography.

** No heavy tar by observation.

heatless drier to produce dry gas for measuring hydrogen sulfide with Draeger tubes. The other stream is partitioned to impinger trains for condensing ammonia and hydrogen chloride in aqueous solutions. Hydrogen sulfide measurements were 190 – 220 ppm, about 50% lower than expected from the sulfur content of the biomass feedstock. This is attributed to absorption by calcined limestone added to the fluidized bed gasifier to control sand agglomeration. Ammonia measurements were 5000 ppm in the raw producer gas.

Since the ballast operates in a cyclic mode, time-resolved gas concentrations are important to assessing the performance of the system. For this purpose, non-dispersive infrared analyzers for CO and CO₂ and an electrochemical cell for O₂ were installed in the gas sampling system (not illustrated in Figure 1). Figure 2 illustrates the continuous data taken during the operation of the ballasted gasifier during the pyrolytic phase of the gasification cycle using these instruments (distinct points are data taken with a gas chromatograph to confirm the continuous measurements). This figure shows how H₂ and CO rapidly increase from virtually zero concentration at the beginning of the pyrolytic phase. Hydrogen peaks almost instantly and gradually declines as the reactor cools while CO continues to climb over most of the pyrolysis phase. Both drop off rapidly after air is readmitted to the reactor (although the persistence of CO in this particular trial indicates that the amount of air

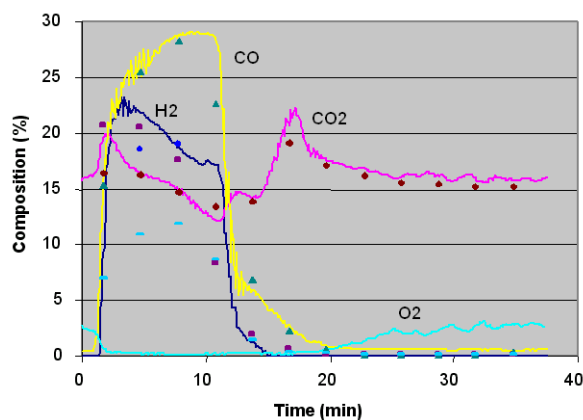


Figure 2. Time Resolved Gas Composition During the Pyrolysis Phase of the Gasification Cycle

added is insufficient for complete combustion of both fresh biomass and residual char in the reactor).

Figure 3 illustrates experimental and simulated cooling curves for the ballasted gasifier after an initial combustion heat-up period followed by the admission of steam (but no biomass) to the reactor. The experimental cooling curve shows a distinct inflection as the result of the heat released from the latent enthalpy stored in the ballast tubes. A simple lumped capacitance (LC) model simulates the experimental data reasonably well except during the period of latent enthalpy change, which appears as an isothermal region in the cooling curve. Modeling work proved this to be an artifact of the LC model. Careful accounting of the growth of a solidification zone within the ballast tubes resulted in the receding interface (RI) model, which produces a more realistic cooling curve, as shown in Figure 3. See Reference 4 for additional details.

Conclusions

- Steam reforming of raw producer gas reduced condensable (heavy) tars to undetectable levels.
- Water-gas shift reactors were successful in reducing carbon monoxide to less than 0.2 vol-%.
- Reliable trace contaminant sampling and measurement was established for ammonia and hydrogen sulfide.
- The thermal ballasting system generated raw producer gas with up to 23 vol-% hydrogen.
- An accurate thermal model of the ballasted gasifier was developed.

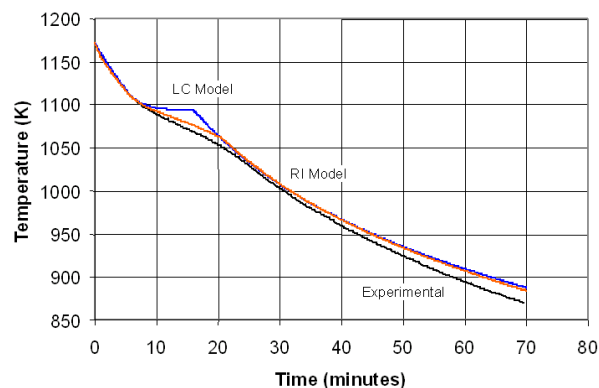


Figure 3. Comparison of Experimental Cooling Curves to Predictions of Thermal Models

FY 2003 Publications/Presentations

1. Zhang, R., Brown, R., Suby, A., and Cummer, K., "Catalytic destruction of tar in biomass-derived producer gas," Energy Conversion and Management (submitted).
2. Zhang, R., Cummer, K., Suby, A., and Brown, R. C., Biomass-derived hydrogen from an air-blown gasifier," Fuel Processing Technology (submitted).
3. Zhang, R., Brown, R. C., and Suby, A., "Thermochemical conversion of switchgrass to hydrogen," Energy and Fuels (submitted).
4. Cummer, R. and Brown, R. C., "Indirectly heated biomass gasification using a latent heat ballast. Part 3: Refinement of the heat transfer model," Biomass and Bioenergy (submitted).
5. Mérida, W., Maness, P., Brown, R. C., and Levin, D. B., "Enhanced hydrogen production and removal of carbon dioxide from indirectly heated biomass gasification," International Journal of Hydrogen Energy (accepted).
6. Zhang, R., Brown, R. C., Suby, A., Cummer, K., "Catalytic cleaning of hot producer gas," Proceedings of the Tenth Biennial Bioenergy Conference, Boise, IA, September 22 – 26, 2002